Recycled selenium in hot spot–influenced lavas records ocean-atmosphere oxygenation

Aierken Yierpan1,*, Stephan König1,*, Jabrane Labidi1,2, Ronny Schoenberg1,3

Oxyg enation of Earth’s oceans and atmosphere through time has consequences for subducted surface signatures that are now stored in the mantle. Here, we report significant mass-dependent selenium isotope variations in modern hot spot–influenced oceanic lavas. These variations are correlated with tracers of mantle source enrichment, which can only be explained by incorporation of abyssal pelagic sediments subducted from a redox-stratified mid-Proterozoic ocean. Selenium geochemical signatures of these sediments have mostly been preserved during long-term recycling and may therefore complement the global surface sediment record as ancient oxygen archives. Combined deep mantle and surface perspectives, together with emerging models for atmospheric oxygen based on selenium systematics, further imply a significantly oxygenated ocean-atmosphere system throughout the mid-Proterozoic.

INTRODUCTION

Earth’s surface oxygenation and mantle evolution are intimately linked by plate tectonics (1–5). Constraints on ocean-atmosphere redox evolution through time are typically obtained from the geochemical signals archived in the surface sedimentary record (6–11). However, most of deep-ocean sediments such as those deposited beyond the continental slopes were likely obliterated from the geological record because of subduction recycling of the oceanic crust (11, 12). Earth’s interior therefore provides complementary clues to secular changes in the surface redox conditions, which impart unique geochemical signatures into the mantle via subduction (13–17). Here, we use selenium (Se) isotopic variations in hot spot–influenced oceanic lavas to infer the recycled Se isotopic and elemental composition of mid-Proterozoic subducted sediments and pyrites. Selenium is a chalcophile redox-sensitive element and exhibits a variety of oxidation states (−2, 0, +4, and +6) in different geological reservoirs (section S1) (18).

Because of the distinct mobility and large isotopic fractionation between different Se species in low-temperature environments, Se isotopic and elemental abundances of marine sediments and sedimentary pyrites have emerged as new redox proxies in the ocean-atmosphere system (section S1 and fig. S1) (7, 18–20). Global marine sediments display large Se isotopic variations, with δ^{82}Se values (deviation in ^{82}Se/^{76}Se relative to the standard) between ~−3 per mil (%) and +3‰ (Fig. 1A). There is a marked shift in sediment average δ^{82}Se toward lighter values from the Precambrian to Phanerozoic (from ~+0.54‰ to ~0.17‰), reflecting Late Neoproterozoic deep-ocean oxygenation (20) (Fig. 1A). By contrast, δ^{82}Se variability in mantle samples is rather limited yet still resolvable (~−0.3‰ to +0.3‰; Fig. 1, A and B). Selenium isotope signatures of mantle reservoirs should be highly sensitive to the presence of recycled sediments, given the large difference in Se contents between the igneous and surface reservoirs (~1 to 2 orders of magnitude difference; Fig. 1A) and the absence of isotope fractionation during high-temperature mantle processes involving Se partitioning between sulfides and silicate melt (section S2) (21).

Fig. 1. Selenium isotope and concentration data for marine sediments and mantle samples. (A) Colored boxes show the mean δ^{82}Se ± 95% confidence interval (CI) and Se contents (log-normal mean ± 1σ) of sediments (N = 759) sorted by age intervals. The group means are calculated over sediment data averaged by depositional age (color-coded filled circles). Top: Gaussian kernel density estimations of sediment δ^{82}Se for each age interval and average isotopic shift (dashed lines). (B) Igneous inventory (N = 87). The shaded field represents the depleted mantle estimate (Table 1). See section S1 for related references.
tracers to study ocean-atmosphere redox evolution recorded by Earth’s surface and interior.

RESULTS
We measured Se isotope composition of selected mid-ocean ridge basalt (MORB) glasses from the southern and northern Mid-Atlantic Ridge (S- and N-MAR; Table 1 and fig. S2). Localized interaction between the S-MAR and Shona and Discovery hot spots resulted in prominent geochemical heterogeneities in the MORB mantle source, highlighting the presence of recycled surface materials (fig. S3). The targeted samples cover a full spectrum of radiogenic isotope variations found in global MORB, ranging from highly depleted to enriched basalts with enriched mantle 1 (EM1), LOMU (low μ; μ = 238U/204Pb), and HIMU (high μ) affinities (Fig. 2; see Supplementary Materials and Methods for details). Selenium isotope compositions of the depleted MAR basalts are within error of the average Pacific-Antarctic Ridge (PAR) mantle that is devoid of any plume contribution (Table 1, Fig. 3, and fig. S4) (21). Together, they define a mean δ82Se of −0.16 ± 0.03‰ [95% confidence interval (CI); N = 31], representing our depleted mantle estimate (section S3). Basalts exhibiting the Discovery and LOMU anomalies extend the depleted mantle range toward heavier δ82Se values, with the Shona anomaly in between (Fig. 3 and section S4). There is a positive correlation between δ34S and δ82Se and δ34S ratios as indicators of mantle source enrichment (Fig. 3). The overall δ82Se variation within the MAR suite (~0.33‰) significantly exceeds the external reproducibility of our method for MORB glasses (~0.08‰, 2 SDs or 2s; Materials and Methods). The calculated mean squared weighted deviation (MSWD) or reduced χ² deviation (MSWD) or reduced χ² test shows that strictly depleted mantle domains have homog- enous Se isotopic compositions (±0.08‰, 2 SDs or 2s; Materials and Methods). The calculated mean squared weighted deviation (MSWD) or reduced χ² test shows that strictly depleted mantle domains have homog-

DISCUSSION
Origin of Se isotopic variability in the mantle
A χ² test shows that strictly depleted mantle domains have homog-

Table 1. Selenium, sulfur, and radiogenic isotope compositions of the MAR glasses. Uncertainties on the sample δ82Se are 95% CI if the number of analyses N ≥ 3, or the 2s external reproducibility of 0.08‰ (estimated for glass matrices) if N ≤ 3. N = number of sample digestions (number in parentheses refers to n).

<table>
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<tr>
<th>Sample Type</th>
<th>Sample</th>
<th>δ82Se (‰)</th>
<th>δ34S (‰)</th>
<th>87Sr/86Sr</th>
<th>143Nd/144Nd</th>
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<tr>
<td>Depleted MORB</td>
<td>EW9309 41D-1g</td>
<td>−0.06 ± 0.08</td>
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<td>EW9309 34D-1g</td>
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<td>0.702111−0.702063</td>
<td>0.51310−0.51328</td>
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*Average δ82Se (±95% CI, N = 27) and Sr-Nd isotopic ratios (±95% CI, N = 66) of PAR glasses [(21, 46) and references therein]; δ34S (±1σ) from (46). †δ82Se (±95% CI, N = 31) is estimated using all the depleted MORBs from the MAR and PAR; δ34S (±1σ) and Sr-Nd isotopic ratios from (15, 27, 48).
The observed correlations between $\delta^{82}\text{Se}$ and $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, and $\delta^{34}\text{S}$ in the S-MAR basalts (Fig. 3 and fig. S5A) cannot be explained by fractionation during mantle melting and/or igneous differentiation (fig. S4 and section S2) (21). Instead, our data require incorporation of enriched plume components with isotopically heavier Se into the ambient asthenospheric mantle. We argue that the enrichment of heavy Se isotopes in the S-MAR can only be achieved by the addition of pelagic sediments, which were previously constrained to have a mid-Proterozoic recycling age between 1 and 2 billion years (Ga) ago based on radiogenic Pb and stable S (both mass-dependent and mass-independent) isotope systems (15, 22, 23). First, most Proterozoic sediments are enriched in $^{82}\text{Se}$ relative to the igneous inventory (Fig. 1A), which would readily satisfy the positive slope of the Se-Sr isotopic mixing relationship (Fig. 3A). Second, the apparent linearity of this trend requires the recycled components to have Se/Sr ratios comparable to the depleted mantle, and only pelagic sediments qualify under such criteria owing to authigenic Se enrichment (Fig. 1A). Assessment of alternative mixing models (see below) lends credence to a broadly linear mixing trend. Other recycled materials that carry EM1, LOMU, and HIMU components in the Discovery and Shona plumes [such as ancient oceanic crust, delaminated subcontinental lithospheric mantle, and lower continental crust (22–24)] have little effect on the Se isotope signature of the MAR mantle source, because either their $\delta^{82}\text{Se}$ are within the igneous inventory range ($\sim$0.3‰ to +0.3‰; $N = 87$) or their Se contents are comparable to the MORB mantle (Fig. 1A and sections S5 and S6). This is similar to the case of S isotope systematics and highlights close geochemical relationship between Se and S during long-term crustal recycling (Fig. 3 and figs. S6 and S7), despite the large differences in the redox potential of these two systems in surface environments (section S4).

Recycled sediments from a redox-stratified ocean

Selenium isotope and elemental systematics of recycled sediments, when interpreted within the previously established framework of marine Se cycle (7, 18–20) (section S1 and fig. S1), may reveal an average global extent of ocean oxygenation over a broad geological time interval. This is because subducted pelagic sediments give an integrated view of those continuously deposited at various depths/redox conditions in an open ocean (fig. S1) over the lifetime of subducting seafloor [e.g., ~50 to 100 million years on average (25) versus Se ocean residence time of $10^4$ years (section S1)]. One might also expect further homogenization of Se within the subducted package during mantle storage for ~1 to 2 Ga if sedimentary sulfides (as the major host of Se) were molten at a range of convective upper mantle conditions (21, 26).

The $\delta^{82}\text{Se}$, $^{87}\text{Sr}/^{86}\text{Sr}$ covariance in our MORB data (Fig. 3A) combined with the previously established model of linear $\delta^{34}\text{S}$-$^{87}\text{Sr}/^{86}\text{Sr}$ relationship (15) and overall similarity between Se and S isotope and elemental behavior during recycling—allows extrapolation...
of the Se content and δ²⁵²Se of recycled sediment using a simple linear mixing model (Figs. 4 and 5; see section S5 for details). An average Se content of 2.45 ± 0.71 μg/g (1σ) is calculated for the recycled sediment using the well-constrained Se/Sr ratio of the depleted mantle and Sr content of recycled sediment (table S3). This value lies close to the +1σ upper bound of the observed sediment average that is essentially identical for the 1- to 2-Ga age interval (0.85 ± 0.61 μg/g; 1σ) and the entire Proterozoic (0.56 ± 0.27 μg/g; 1σ; Fig. 5B). This argues against a significant, if any, Se loss (or modification of Se/Sr ratio) and hence associated isotopic fractionation from bulk sedimentary lithologies during subduction in the mid-Proterozoic and large-scale recycling in the mantle, reminiscent of that suggested for S (15) (see section S5 for discussion of more lines of evidence). Extrapolation of the linear regression to a model composition of 1.5-Ga-old recycled sediment $^{87}$Sr/$^{86}$Sr = 0.7203 (15, 22, 24, 27) yields δ²⁵²Se = +1.44 ± 0.39‰ (95% CI; Fig. 4B). This value, although not uncommon in mid-Proterozoic sediments, is similar to or heavier than the +1σ upper bound of the observed average for the 1- to 2-Ga interval (+0.62 ± 0.50‰; 1σ, N = 76) or the entire Proterozoic (+0.53 ± 1.13‰; 1σ, N = 210) (table S3 and Figs. 4B and 5A). This is reassuringly consistent with recycled pelagic sediments from a redox-stratified ocean (9), where the subduction of oceanic plate was predominantly associated with deep-ocean sediments deposited on the abyssal seafloor beyond the continental slope settings [e.g., (12)]. These abyssal sediments would be characterized by the highest δ²⁵²Se because of near-quantitative reduction of water-soluble Se oxyanions under anoxic conditions, following partial reduction under oxic/suboxic conditions at shallower water depth (section S1 and fig. S1).

We further assess the applicability and robustness of the simple linear mixing model for characterization of the recycled sediment reservoir. Considering that the amount of sediment added to the S-MAR mantle is small [up to ~1 weight % (wt %) in our model; see also (15, 24)], the δ²⁵²Se - $^{87}$Sr/$^{86}$Sr array within the MORB data range...
might only represent a small segment of a hyperbolic mixing curve (Fig. 4B). Besides, Se content and δ82Se of the sediment end member cannot be independently determined. The permissible range of these two variables, however, can be constrained. Our mixing models with the known range of 1- to 2-Ga-old sediment compositions (mean ± 1σ) show that a realistic Se content and δ82Se of recycled end member in the S-MAR source must be both at least comparable to the +1σ upper bound of observed sediment averages (Fig. 4B). This result provides strong support for the idea (see above) that there was insignificant Se modification during sediment subduction and that recycled sediments dominantly reflect "abyssal" δ82Se signature at the surface. Moreover, all the mixing arrays compatible with our MORB data and observed sediment averages (δ82Se up to +2σ upper bound) lie well within 95% CI range of the linear extrapolation (Fig. 4B), which, in turn, implies that the recycled sediment composition may be adequately estimated by a broadly linear mixing model. Accordingly, the possible δ82Se range of recycled sediment calculated from the observed δ82Se-87Sr/86Sr relationship at other reasonable recycling ages between 1 and 2 Ga (table S3) would also remain realistic for subducted sediments associated with prevalent deep-ocean anoxia (9) and hence does not alter our interpretation (Fig. 5A and section S5).

**Mantle recycling record of atmospheric oxygenation**

Subduction removed large portions of deep marine pyrites from the surface and thus transferred a significant Se reservoir into the deep-mantle source of our hot spots. This "lost-and-resurfaced" abyssal Se record complements the shallower marine pyrite record preserved on Earth’s surface, which was used for reconstruction of the ocean-atmosphere redox evolution (Fig. 5, C and E) (7, 19, 28). Combining our result for the recycled sediment Se content (2.45 ± 0.71 μg/g; 1σ) with the mean pyrite-bound S content of 1- to 2-Ga-old sediments [1.1±1.4 wt %; 1σ, N = 85; (10, 29)] and mean pyrite/matrix Se ratio of ~5.82 observed for sediments of all ages (19), we estimate a range of Se content between 13±4 and 119±155 μg/g (1σ) for the recycled pyrite. This range depends on the relative contributions of pyrite and other matrices (organic matter, clay, and other silicates) to bulk Se budget in global black shales (section S5 and Fig. 5C). A more realistic value probably tends toward our “lower estimate” because of the greater fraction of organic-bound Se in the mid-Proterozoic sediments compared with Phanerozoic sediments, where more abundant Se might be incorporated into pyrites after dissimilatory reduction of Se oxyanions in seawater (20). Invoking nonlinear mixing relationships between the depleted mantle and sediment would lead to different results for Se content of recycled pyrite, and its minimum possible range is calculated at fixed δ82Se values of 1σ and 2σ above the observed mean of 1- to 2-Ga-old sediments (Fig. 4B and fig. S8; see section S5 for details). All these mixing models yield a “lower estimate” of recycled pyrite Se content that is comparable within error to the observed average of sedimentary pyrites formed during the 1- to 2-Ga interval (19,±31 μg/g) or entire Proterozoic [16±30 μg/g, 1σ; (7, 19, 28)] (table S3 and Fig. 5C and fig. S8).

The notable similarity between the recycled abyssal and surface pyrite Se signatures from different depositional/redox environments lends additional support to the representativeness of Se in surface pyrites, although shallower, for atmospheric oxygen modeling (Fig. 5, C and E) (7). In turn, within the framework of the Large et al. (7) model, our Se concentration estimates for the recycled, abyssal pyrite support the idea of high atmospheric oxygen levels over an extended time interval (~50 to 100 million years; see above) in the mid-Proterozoic [on average, ~30 to 60% present atmospheric level (PAL); Fig. 5E]. Such a high oxygen estimate in (7) contrasts with earlier suggestions ranging from <0.1% to >4% PAL (30–34), with the most widely accepted range of ~0.01 to 10% PAL (8) (Fig. 5E); note, however, that it still remains lower than the threshold values required to sustain a fully oxygenated abyssal ocean (~70 to 80% PAL; (35), consistent with the well-established mid-Proterozoic
MATERIALS AND METHODS

Samples and chemical procedures

For this work, we selected a suite of well-characterized submarine glasses collected along the MAR (S- and N-MAR, N = 18; Fig. S2). They include 14 enriched MORBs from the S-MAR interacting with the Discovery and Shona plumes and 2 depleted MORBs from each section of the MAR devoid of plume contribution. This is supplemented by the published $^82$Se data for PAR depleted MORBs (N = 27) (21). In addition, we report on $^82$Se measurements of three well-characterized granitoids from the Västervik area in Sweden, resembling materials derived from the mid-Proterozoic continental crust. See the Supplementary Materials for a detailed description of the geochemical background of the samples.

The sample digestion followed the method of (41). Samples were mixed with $^{74}$Se-$^{75}$Se double spike and $^{125}$Te spike and dissolved in an HF-HNO$_3$ mixture. This was followed by successive dissolutions and evaporations with HCl to eliminate the isobaric interference Ge. Samples were subsequently processed through anion and cation exchange chromatography for Se and Te purification. In the anion exchange column, Se was eluted following two different protocols, namely, “HCl chemistry” (41) and “HF chemistry” (this work). See the Supplementary Materials for full details.

Isotopic measurements

Concentrations of Se (when unknown) and Te were determined via the isotope dilution method on a Thermo Fisher Scientific iCAP-Qc inductively coupled plasma mass spectrometer (ICP-MS) linked with an ESI hydride/ICP hydride generator (41). Selenium isotopes were analyzed on a Thermo Fisher Scientific NeptunePlus multicollector ICP-MS linked with an HGX-200 hydride generator (42). Before the final isotope measurements, sample solutions (1 ml of 2 N HCl) were monitored for residual Ge and further evaporated at 85°C in case of any detectable Ge (41). Procedural blanks (N = 4) were also checked at this stage, which yielded background signal intensities for all Se isotopes. Each sample analysis was bracketed by spiked NIST SRM 3149 standard (30 ng/ml), and Se isotope composition is reported relative to NIST SRM 3149 in ‰ units using $^82$Se notation

$$
\delta^{82}\text{Se}_{\text{sample}} = \frac{(^{82}\text{Se} / ^{76}\text{Se})_{\text{sample}}}{(^{82}\text{Se} / ^{76}\text{Se})_{\text{NIST SRM 3149}}} - 1
$$

Most sample solutions contained ~10 to 35 ng of Se, which typically yields an internal error of <0.07‰ (95% CI based on 40 cycles of integration) for an individual measurement (tables S1 and S2). The interlaboratory standard MH-495 (30 ng/ml) included in each analytical session for quality control gives $\delta^{82}\text{Se} = -3.25 \pm 0.07$‰ (2s, n = 53), identical to literature data obtained under intermediate precision conditions (table S2). Together, these data allow us to estimate the 2σ analytical precision of our method and yield an average $\delta^{82}\text{Se} = -3.25 \pm 0.07$‰ (2s, n = 200; table S2).

Several international rock standards processed together with the samples in this study are listed in table S1. The $\delta^{82}\text{Se}$ values of USGS (U.S. Geological Survey) rock standards BHVO-2 ($n = 4$), BCR-2 ($n = 1$), BIR-1a ($n = 1$), and W-2a ($n = 2$) are all in excellent agreement with the literature data. We additionally report on analyses of other certified rock standards JG-1, MRG-1, and JA-3. The external reproducibility of our method for nonglass matrices is evaluated by pooling over all replicate analyses of rock standards (each >3 times) under intermediate precision conditions (e.g., (43)).
where $s_p$ is the pooled SD, $N$ is the number of different samples, $n_i$ is the number of replicate analyses of a sample, and $\delta_{ij}$ and $\bar{\delta}_i$ are the individual and average $\delta^{82}\text{Se}$ of a sample, respectively. This approach requires a homogeneity of variances across $N$ groups of samples. This is validated by running a Bartlett’s test over 52 analyses (51 digests) of five rock standards, which yields a test statistic of 0.78 and a p value of 0.94. Using Eq. 2, we obtained an external reproducibility of $2s_p = \pm 0.12\%$ for $\delta^{82}\text{Se}$ data of nonglass samples (table S1).

As for glass matrices, a recent study on PAR MORB reported higher reproducibility of $2s = 0.09\%$ on $\delta^{82}\text{Se}$ (21). To reevaluate our method reproducibility for glasses given the larger dataset here, we combined $\delta^{82}\text{Se}$ data from replicate analyses ($>3$ times) of three MAR glasses, which were randomly selected and processed via two different purification protocols, and the previously reported PAR MORB data (table S2). These groups of samples ($N = 4$, $n_i = 23$) passed the null hypothesis of the Bartlett’s test with a test statistic of 1.57 and a p value of 0.67. Therefore, Eq. 2 can be used to calculate the pooled external reproducibility, which yields $2s_p = \pm 0.08\%$. This is similar to the analytical precision (±0.07‰) and is considerably lower than ±0.08‰ if $\delta^{82}\text{Se}$ text and tables, the quoted uncertainty on a MORB to the analytical precision (±0.07‰) and is considerably lower than ±0.08‰ if $\delta^{82}\text{Se}$ data of nonglass samples (table S1).

$\bar{\delta}_i = \frac{1}{n_i} \sum_{j=1}^{n_i} \delta_{ij}$

$\delta_{ij}$ are the individual $\delta^{82}\text{Se}$ of a sample, respectively. This approach requires a homogeneity of variances across $N$ groups of samples. This is validated by running a Bartlett’s test over 52 analyses (51 digests) of five rock standards, which yields a test statistic of 0.78 and a p value of 0.94. Using Eq. 2, we obtained an external reproducibility of $2s_p = \pm 0.12\%$ for $\delta^{82}\text{Se}$ data of nonglass samples (table S1).

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$\delta_{ij}$ are the individual $\delta^{82}\text{Se}$ of a sample, respectively. This approach requires a homogeneity of variances across $N$ groups of samples. This is validated by running a Bartlett’s test over 52 analyses (51 digests) of five rock standards, which yields a test statistic of 0.78 and a p value of 0.94. Using Eq. 2, we obtained an external reproducibility of $2s_p = \pm 0.12\%$ for $\delta^{82}\text{Se}$ data of nonglass samples (table S1).

As for glass matrices, a recent study on PAR MORB reported higher reproducibility of $2s = 0.09\%$ on $\delta^{82}\text{Se}$ (21). To reevaluate our method reproducibility for glasses given the larger dataset here, we combined $\delta^{82}\text{Se}$ data from replicate analyses ($>3$ times) of three MAR glasses, which were randomly selected and processed via two different purification protocols, and the previously reported PAR MORB data (table S2). These groups of samples ($N = 4$, $n_i = 23$) passed the null hypothesis of the Bartlett’s test with a test statistic of 1.57 and a p value of 0.67. Therefore, Eq. 2 can be used to calculate the pooled external reproducibility, which yields $2s_p = \pm 0.08\%$. This is similar to the analytical precision (±0.07‰) and is considerably lower than ±0.08‰ if $\delta^{82}\text{Se}$ text and tables, the quoted uncertainty on a MORB to the analytical precision (±0.07‰) and is considerably lower than ±0.08‰ if $\delta^{82}\text{Se}$ data of nonglass samples (table S1).

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